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CONTROL OF MASS TRANSPORT OF DISSEMINATED LIQUIDS AND VAPORS: CROSS-LINKED POLYMERIC PARTICLE SURVEY AND SORPTION EXPERIMENTATION

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An initial evaluation was performed in preparation for new investigations comparing monolithic cross-linked polymeric particles with continuum viscoelastic fluids for control of liquid breakup and mass transport. This evaluation reports the survey results on past polymeric particles studied. The test liquids employed with viscoelastic additives were identified. These liquids were employed in sorption experiments to identify candidate polymeric particles for further experimentation. Polymer phase diagram theory was employed to predict soluble/sorptive systems and all predictions correctly yielded sorbed particles.

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PREFACE

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CONTROL OF MASS TRANSPORT OF DISSEMINATED LIQUIDS AND VAPORS: CROSS-LINKED POLYMERIC PARTICLE SURVEY AND SORPTION EXPERIMENTATION

1. INTRODUCTION

1.1 Classification of Mass Transport Control Mechanisms.

A general mass transport process exists that consists of transfer of a bulk mass of fluid to a fluid dispersed over a predefined surface area. The scale of this process can range from small enclosed, industrial processes to large dispersals over large areas of the environment.[1] Strategies and mechanisms for control of this mass transport process can be divided into those mechanisms that employ additives to alter the fluid properties or geometry and those that employ the unaltered fluid. The additives employed can be further divided into the following two classes:

- Monolithic additives control the structure and/or geometry of the fluid at the smallest geometrical unit of mass transport (e.g., particles and other carrier structures).

- Continuum additives alter the fluid properties (i.e., viscoelasticity and surface tension) that control mass transport but do not impose a prestructured particle size or geometry on the fluid.

Given these classifications of fluid mass transport mechanisms, one can define the scope of this review and investigation as limited to that of control by monolithic additives. A brief survey of the advantages and limitations of each class will be given. A further classification of monolithic additives will be provided based on composition (e.g., cross-linked polymers, porous inorganic particles), geometry (spherical, disk, rod), and mechanical properties (deformable, brittle).

1.2 Review.

Several general references on mass transport control are listed in the bibliography section. Also listed in the bibliography are more specific publications involving research in our laboratories with cross-linked polymer particles, often called imbiber beads (Dow Chem, Midland, MI) or sorptive particles.

The chemicals that had approvals for chamber and environmental testing were reviewed. Those chemicals with existing data sets on dissemination control with continuum additives were identified for comparative experimentation with monolithic cross-linked polymer additives. The test chemicals identified were triethylphosphate (TEPO), tributylphosphate (TBPO), and dibutylphthalate (DBP).

2. EXPERIMENTATION

2.1 Materials.

- Polymeric Materials.

Previous research on particles was reviewed and an inventory of selected cross-linked particles is provided in Table 1. The first column identifies the polymer composition, identification, and lot number; and the second column lists available information on particle size. The next column provides general remarks on source or preparation; the quantity of limited experimental samples is also provided.

2.2 Chemicals.

The chemicals employed as environmentally and/or safety approved dissemination test fluids and sorbates for the polymeric materials are listed in Table 2. The chemical name, code, and source are listed in the sequential columns.

2.3 Procedures.

The predictive methods were based on polymer phase diagram theory.[2,3] The experimental procedure followed ASTM D3132.[4]

3. RESULTS

- Polymer-Liquid Interaction Screening Experiments.

One initial set of experiments in mass transport studies involves selecting polymer-liquid pairs for study employing theoretical phase diagram calculations and confirmatory experiments.[5] A set of sorption screening experiment results are recorded in Table 3. The codes for the polymer-liquid pair are listed in the first column and sorption results are noted in adjacent column(s). All candidate polymer-liquid pairs resulted in soluble/sorbed systems, confirming the phase diagram predictions.

4. DISCUSSION AND CONCLUSIONS

The formulation, rheology, and breakup of viscoelastic and particulate dissemination fluids have been extensively studied in our laboratory; however, a direct comparison at ultra-high stress rates has never been an issue. In preparation for ongoing studies comparing viscoelastic versus particulated dissemination mechanisms, distinction has been drawn between these two transport control mechanisms. The environmentally approved test liquids employed with viscoelastic additives in previous test programs were identified. Polymer phase diagrams were employed to predict and select candidate sorptive polymers. All predictions were successful and resulted in sorption into the cross-linked candidate polymers. Therefore, several candidate systems of sorbed particles in test liquids are now available for comparative dissemination testing and mass transport experimentation.

Table 1. Cross-Linked Polymeric Particles Employed to Control Fluid Mass Transport

Polymer Particle Composition/Lot	Code	Size	Remarks	Quantity Available
Dow Imbiber Bead TC Lot 08689-38	DIB-TC	>20 mesh		20 g
Dow Imbiber Bead T-32	DIB-T32			10 g
Dow Imbiber Beads - S No. S-0110.52	DIB-S	~500 m	1974	100 g
Dow Imbiber Bead T32 poly(t-butyl styrene)	DIB-T32	1 mm		50 g
Dow Imbiber Bead Lot N, FPS 400ZL-PTBS	DIB-FPS			
Dow Imbiber Bead T Lot XE-01-00-31	DIB-T	<200		20 g
Dow Imbiber Beads T	DIB-T 2mm	2 mm	Experimental Lot	
Dow Imbiber Beads T	DIB-TXE	>>3-5 mm		
Dow Imbiber Bead S	DIB-S			500 g
Dow Imbiber Bead TC	DIB-TC			400 g
Dow Imbiber Bead T	DIB-T			400 g
LU-Bust 3080-1	LU-BUST1		Lehigh U.	
LU-Bust 3080-2	LU-BUST2		Lehigh U.	
Poly(50% vinylacetate-co-50% m-vinyl pyrollidine-co <1.0% DVB)	PVA-PVP	1/4 Rods	Lehigh U. 1984	200 g
Poly(butylmethacrylate-co-.02 vol % DVB)	PIBM-Bulk	1" dia	LTC Kopchick Bulk polymerized	3 beads
Poly(methylmethacrylate)	PMMA	1"	LTC Kopchick Bulk polymerized	1 bead each
Poly(MMA-co-acrylate)	PMMA-Ac			
Poly(methylmethacrylate) Shock Hydrodynamic Run 8	PMA-SH	10 beads		
Poly(MMA-co-styrene) NAS Beads	PMMA-S	Small		500 g
Sustrelle Microbeads		<75 m	Aqueous	

Table 1. Cross-Linked Polymeric Particles Employed to Control Fluid Mass Transport (Continued)

Poly(styrene-co-0.02-DVB) P649002PN, Lot L900531A	PS-Bng	650 μ	1000 μ max	1 kg
Polystyrene CT-Macrobead 1/4	PS-MB	5 mm	Not cross-linked	100 g
Polystyrene Cross-Linked Rods Goodfellow Corp.	PS-Rod	> 10 mm	Cut from rods	

Table 2. Chemicals Employed in Sorption Screening Experiments

Chemical	Code	Source
Triethyl phosphate	TEPO	Aldrich
Tributyl phosphate	TBPO	Ashland
Dibutyl Phthalate	DBP	Aldrich

Table 3. Sorption Screening Experimental Results for Polymer-Liquid Pairs: Tributylphosphate (TBPO) Example

Liquid Code	Polymer Code (see Table 1)	Predicted Interaction (S = Sorption)	Sorption Results
TBPO	DIB-TXE	S	S
TBPO	DIB-T 2 mm	S	S
TBPO	PS-Bng	S	S
TBPO	LU-BUST1	S	S
TBPO	LU-BUST2	S	S
TBPO	PS-Bng	S	S
TBPO	PIBM-Bulk	S	S
TBPO	PS-MB	S	S, dissolved

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